(D1)

PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G01N 33/34, D21C 9/10	A1	(11) International Publication Number: **WO 96/12183** (43) International Publication Date: 25 April 1996 (25.04.96)

(21) International Application Number: PCT/EP95/04030

(22) International Filing Date: 10 October 1995 (10.10.95)

(30) Priority Data:
9403520-1 14 October 1994 (14.10.94) SE

(71) Applicant *(for all designated States except US)*: EKA NOBEL AB [SE/SE]; S-445 80 Bohus (SE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: RENBERG, Lars [SE/SE]; Okgränd 5, S-137 38 Västerhaninge (SE). SPAREN, Anders [SE/SE]; Alemar, Wadmangatan 6, S-412 53 Göteborg (SE).

(74) Agents: BERGVALL EFTRING, Stina, Lena et al.; Dr. Ludwig Brann Patentbyrå AB, P.O. Box 17192, S-104 62 Stockholm (SE).

(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: A METHOD OF DETERMINING THE ORGANIC CONTENT IN PULP AND PAPER MILL EFFLUENTS
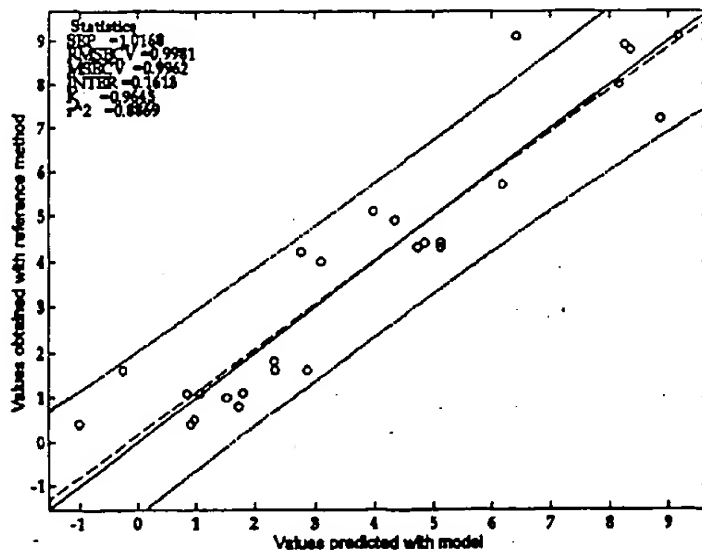
(57) Abstract

A method, based on UV/VIS/NIR/IR (including Raman spectroscopy), for the qualitative and quantitative determination of quality parameters in pulp and paper and/or the organic content in effluents from pulp and paper production, by applying chemometric methods.

A METHOD OF DETERMINING THE ORGANIC CONTENT IN PULP AND PAPER
MILL EFFLUENTS

FIELD OF THE INVENTION
The present invention is directed to a method for qualitative
and quantitative determination of various parameters
reflecting the pulp or paper quality and environmental impact
of pulp and paper production, and more particularly to a
spectroscopic method for the instantaneous and continuous
analysis of the various parameters reflecting the quality of
the pulp and paper as well as the environmental impact of the
effluents paper, performed on the aqueous phases from the
process stages in a pulp mill or paper mill.

BACKGROUND OF THE INVENTION
The main constituents of wood are cellulose, hemicellulose,
lignin and extractives. The quality of pulp or paper is
strongly related to its content of cellulose i.e a higher
cellulose content increases the quality. Especially lignin,
which is an aromatic crosslinked polymer, is an unwanted
constituent in the pulp and affects the quality of the pulp
negatively. In chemical pulp production the major part of the
lignin is removed in the cooking process.

The remaining lignin is removed in a process, referred to as
bleaching, by chemical oxidation. The bleaching process
consists usually of 3-5 stages. Examples of oxidation
chemicals used for bleaching are molecular chlorine, chlorine
dioxide, hydrogen peroxide and ozone. Usually an alkaline
extraction stage is employed between the different oxidation
stages. From each bleaching stage an aqueous discharge is
obtained, containing the degradation products of mainly
lignin. This water soluble organic material reflects the
mechanisms and removal efficiencies of the oxidation
processes.

The bleached pulp is characterized by e.g. the kappa number, paper whiteness, measured as ISO-90 or similar parameters, paper strength, commonly measured as viscosity, tear index, tensile index or burst index.

The measurement of the kappa number in the aqueous phase is a relatively crude measurement of the reduction in the lignin content after each stage. According to the Technical Association of Pulp and Paper Industries (TAPPI) the kappa number reflects the relative hardness, bleachability or degree of delignification. The kappa number is defined as the degree of consumption of potassium permanganate (TAPPI Standard Method T 236 cm-85). Another, very similar and standardised method methods is SCAN-C 1:77.

The viscosity is a surrogate parameter reflecting the pulp strength and is often used instead of the more tedious determination of paper strength by tear index, tensile index and burst index.

Another important quality parameter is the whiteness or the brightness of the pulp and paper, which usually is measured as ISO-90.

The environmental impact of pulp and paper mill effluents is often assessed using parameters reflecting the organic content. Such parameters are the chemical oxygen demand (COD), the biological oxygen demand (BOD 5, BOD 7 and BOD 28), the total organic content (TOC), the colour of the effluent, adsorbable organohalogenes (AOX), suspended organic material and washing losses, the latter expressed as COD or sodium sulphate.

One major drawback with methods according to prior art of monitoring the efficiency of the bleaching process is the delay between the sampling of the bleach plant effluent and the determination of the kappa number and other conventional

3

parameter, currently in use.

This delay may lead to important quality losses as appropriate
measures are unnecessarily delayed. Another disadvantage with
prior art methods are that the characteristics and
distribution of this chemically very complex organic material
is not very well described by these simple methods. It is
obvious that there is a definite need for more convenient and
relevant methods for characterising the quality of the pulp
and the organic material in pulp mill effluents. The present
invention has for object to offer a solution to the mentioned
and similar problems, by providing a method that allows the
continuous monitoring of pulp mill effluents during the pulp
and paper mill process. This object is attained by the
combined use of spectrometric and chemometric techniques.

According to the invention, the aqueous effluent is submitted
to spectrometric analysis. However, the water-soluble organic
material represents a multi-component system or a system
having a high degree of background interferences which greatly
complicate the problem of spectrometric analysis.

The use of multivariate data analysis in the characterisation
of multi-component systems is presently a field of develop-
ment. Applied generally to the field of chemistry, and parti-
cularly to the field of analytical chemistry, those several
statistical methods are also termed chemometric methods,
forming the discipline of chemometrics. The technique of
chemometrics is more fully explained in S.D. Brown, "Chemomet-
rics", Anal. Chem. 62, 84R-101R (1990), which by reference is
incorporated herein in its entirety.

Brown et al, in the US patent 5,121,337 (1990) disclose a
method, based on multivariate data analysis, for correcting
spectral data for data due to the spectral measurement process
itself and estimating unknown property and/or composition data
of a sample using such method.

4

Richardson et al, in US 5 242 602 (1992) disclose a method for
simultaneously analyzing the concentration of performance
indicators in aqueous system by determining an absorbance or
emission spectrum in a wavelength range of 200 to 2500 nm and
applying chemometric algorithms to the absorbance or emission
spectrum. Said performance indicators are selected from scale
inhibitors, corrosion inhibitors, lubricants, metal working
fluids, pH regulators, dispersants, defoaming agents, seque-
strants, biocides, detackifiers, and precipitating agents. The
concentrations of the performance indicators determined by the
chemometric algorithms are compared to predefined ranges for
the respective performance indicators.

However, the combination of simultaneously measuring several
wavelengths of a liquid sample and applying chemometric tech-
niques has been described and applied as a general technique.
For example, Hewlett-Packard, a commercial company which is
manufacturing chemical-analytical instrument, discusses the
importance of chemometrical methods for multicomponent
analysis using multiwavelength spectroscopy in its booklet
"The diode-array advantage in UV/Visible Spectroscopy"
(Hewlett Packard Co, publication no.12-5954-8912,1988).

SUMMARY OF THE INVENTION
None of the above mentioned authors suggests how to solve the
problem of the qualitative and quantitative determination of
the various parameters related to pulp and paper production
such as the lignin content reflected in the kappa number; the
parameters reflecting the paper strength such as the visco-
city, tear index, tensile index and burst index; brightness
measured as ISO-90; or the parameters reflecting the organic
content in the effluents, such as chemical oxygen demand
(COD), washing losses expressed as COD or sodium sulphate, the
total organic content (TOC); and the biological oxygen demand
(BOD 5, BOD 7 and BOD 28); colour, suspended solid material,
adsorbable organohalogenes (AOX), washing losses expressed as
COD or sodium sulphate in a way permitting the continuous

monitoring of this parameters. This, however, is the object of
the present invention, which provides a reliable and precise
way of monitoring the content of organic material or parame-
ters reflecting the change in quality of the pulp or paper by
a rapid chemical analysis coupled with multivariate data
analysis using the technique of chemometrics.

DETAILED DESCRIPTION OF THE INVENTION

One object of the invention is to provide a method for the
estimation of the difference in kappa number in pulp mill
effluents before and after one or several process stages by
measuring the organic content in the aqueous phase.

It is another object of the invention to provide a method for
the estimation of the difference in paper strength, measured
as the viscosity value, tear index, tensile index or burst
index, before and after a process stage by measuring the
organic content in the aqueous phase in pulp mill effluents.

Yet another object is the estimation of the difference in
paper whiteness or brightness measured as ISO-90 or similar
parameters before and after a process stage by measuring the
organic content in the aqueous phase.

The invention also comprises methods for the direct and
instantaneous determination of chemical oxygen demand (COD),
wash losses defined as COD or sodium sulphate, total organic
carbon content (TOC), biological oxygen demand e.g. BOD 5, BOD
7, and BOD 28 as well as adsorbable organic halogenates (AOX),
suspended solid material and colour in the aqueous phase in
the pulp mill effluents. The invention also includes the
determination of groups of chemically similar compounds, e.g.
extractives, lignin residues and carbohydrates.

The above objects of the invention are obtained by a method of
measurement of organic material in the aqueous phase of pulp
and paper mill effluent by analysing the ultraviolet, visible,

6

near-infrared and/or infrared (incl. Raman spectroscopy) spec-
trum of the paper/pulp in the process line in a wavelength
range within 180 nm to 400 μm and applying chemometric evalua-
tion of the spectrum to calculate the difference in quality
parameters, e.g. kappa number, and direct determination of
organic content, e.g. COD.

According to the invention it has now, by an extensive deve-
lopment work, been shown that it is possible to directly and
continuously detect the absorption, transmittance or
reflectance spectra in the above defined parameters and
particularily the kappa number in the pulp and/or COD in pulp
mill effluent using a UV/VIS/NIR/IR (including Raman
spectroscopy) spectrometer and, by the use of absorbance or
transmittance values at discrete wavelengths from these
spectra, calculate the above defined parameters, especially
the kappa number, the difference in paper strength measured as
viscosity, tear index, tensile index, burst index or similar
parameters; the difference in paper whiteness or brightness
measured as ISO-90 or similar parameters, before and after a
process stage. Further objects are the direct determination of
the chemical oxygen demand (COD), wash losses expressed as COD
or sodium sulphate, total organic content (TOC), as well as
the biological oxygen demand (BOD 5, BOD 7, and BOD 28),
adsorbable organic halogenates (AOX), suspended solid material
and colour. Also the direct determination of chemically
similar compounds can be carried out. Examples of such groups
are extractives, lignin residues and carbohydrates.

The terminology pulp used herein refers not only to bleached
pulp and/or paper, but also to unbleached or partially bleac-
hed mechanical or chemical pulp.

Technically, the spectrometric analysis can be performed by
on-line, in-line or at-line detection and carried out as a
continuous monitoring, by use of an on-line, in-line or at-
line optical fibre probe, or by taking individual samples for

7

separate analysis. In all cases, absorption, transmittance or
reflectance spectra are subject to further data treatment
using values from several discrete wavelengths from each
particular spectrum.

The spectral information reflects a variety of properties of
the organic content. Depending on the parameter of interest
relevant and selected spectral information is correlated to
the specific parameter.

An example of such a technique is the use of a device, placed
at a distance from the process, containing a light source,
detector, electronic components and other necessary components
to transmit a signal through an optical fibre to the sample,
where the light is transmitted through or reflected on or
partly through the sample. The resulting signals are returned
to the detector in an accompanying optical fibre cable, and
recorded.

In the spectrometer, the light is converted into an electric
signal which is then conveyed to a computer where the spectrum
of a previously stored reference scan can be related to, e.g.
subtracted from, the sample spectrum and a reference corrected
spectrum is calculated.

Another example is by manually or automatically taking samples
at relevant time intervals and submitting the samples to
analysis in an analytical instrument, containing the light
source, detector, electronic components and other necessary
components. The absorption, transmittance or reflectance
spectra are then subjected to further data treatment, using
values from several discrete wavelengths from each particular
spectrum.

It is preferred that the detector has a measuring interval of
at the most 10 nm, preferably 2 nm, and most preferably 1 nm
or less. The detection is performed in the UV/VIS/NIR/IR

8

(including Raman spectroscopy) wavelength range of 180 nm to 400 μm.

This can be accomplished by the use of a scanning instrument, a diode array instrument, a Fourier transform instrument or any other similar equipment, known to the man skilled in the art.

An evaluation of wavelengths which contain absorption, transmittance or reflectance provides features relevant for the analysis. By the application of chemometrical methods to the obtained spectra it is then possible to ignore wavelengths which do not contain information that contribute to the analysis, even though the measurement will include information from the entire wavelength range.

The determination and control of *e.g.* the reduction in kappa number of paper in pulp and/or paper by use of the spectro-metric measurements comprise two main steps, the first of which being the development of a calibration model, involving the substeps of development of learning sets; data processing; and data analysis, by the use of pulp and/or paper samples of known kappa numbers. The second main step is the spectrometric analysis of the sample of the unknown kappa number, spectral data processing, optionally followed by data analysis; and application of the calibration model, developed in the first main step, to the thereby obtained data.

(I) DEVELOPMENT OF A CALIBRATION MODEL

The kappa number is measured in the traditional way (TAPPI T 236 cm-85 (1984) or SCAN-C 1:77) for a number of pulp samples before and after a process stage. The difference of the kappa number, before and after the process stage, is then used in the development of a calibration model wherein the three substeps discussed below are applied to the registered absorption, reflectance or emission spectra of said samples.

(I.a) Development of learning sets
Model learning sets consist of a large number of absorption,
transmittance or reflectance spectra from the samples with
known kappa number characteristics, that preferably should be
representative of the production line. The learning sets are
used in the chemometric algorithms to calculate the resulting
model parameters.

(I.b) Data processing
To reduce noise and adjust for base line drift the spectral
raw data should be processed. This processing may also reveal
hidden information, such as identity of apparently dissimilar
spectra or non-identity of apparently very similar spectra.

Moreover, the assumptions leading to Beer's law (stating that,
for a given absorption coefficient and length of the optical
path in the absorptive media, the total amount of light absor-
bed is proportional to the molecular concentration of the
sample) are not always fulfilled in the complex system that
the pulp mill effluent sample constitutes. This is due to a
number of factors, such as the high concentrations, often
found in industrial samples. Another complication factor is
light scattering variations, depending on particles in the
sample.

Various theories have been developed to overcome this problem
and the most used are: the Kubelka-Munk transformation (P.
Kubelka, F. Munk, Z. Tech. Physik 12, 593 (1931)), which takes
account of absorption and scatter; and the Multiplicative
Scatter Correction (P. Geladi, D. MacDougall, H. Martens,
Appl. Spect. 39, 491-500 (1985)) where each spectrum is 'cor-
rected' in both offset and slope by comparing it to an 'ideal'
spectrum (the mean spectrum).

The Kubelka-Munk transform is according to Eq. 1:

$$A_{ik} = \frac{(1-R_{ik})^2}{2R_{ik}} \tag{1}$$

10

where R_{ik} is the apparent absorbance at the wavelength k, A_{ik} is the transformed absorbance at the wavelength k, and the index i represents the sample spectra available.

The Multiplicative Scatter Correction (MSC) is according to Eq. 2:

$$A_{ik} = \frac{R_{ik} - \hat{a}_i}{\hat{b}_i}$$

(2)

where A_{ik}, R_{ik}, i and k have the same meanings as above, $\hat{a}_i$ is the least squares estimation of the intercept parameter, and $\bar{b}_i$ is the least squares estimation of the slope parameter. Another way of linearising the spectral data also is by use of derivatives, e.g. up to the fourth order derivatives (A. Savitzky, M.J.E. Golay, Anal. Chem. 36, 1627-1639 (1964)). The derivative of the spectrum results in a transformed spectrum, consisting only of the relative changes between the adjacent wavelengths, and it has been shown that the peak intensities of derived spectra tend to be more linear with concentration (T.C. O'Haver, T. Begley, Anal. Chem. 53, 1876 (1981)).

Linearisation can also be accomplished by use of the Fourier transformation, or by use of the Standard Normal Variate transformation as disclosed in R. J. Barnes, M. S. Dhanoa and S. J. Lister, Appl. Spectrosc., Vol. 43, number 5, pp. 772-777 (1989).

(I.c) Data analysis
Data analysis using chemometric techniques then allows the calibration model to be developed. There are several chemometric techniques which can be used, such as Principal Component Analysis (PCA), Partial Least Squares Regression (PLS), Principal Components Regression (PCR), Multilinear Regression Analysis (MLR) and Discriminant Analysis. The preferred chemometric technique according to the invention is the PLS method.

(I.c.1) Principal Component Analysis (PCA)

By PCA, a set of correlated variables is compressed into a smaller set of uncorrelated variables. This transformation consists of a rotation of the coordinate system, resulting in the alignment of information on a fewer number of axes than in the original arrangement. Hereby, the variables that are highly correlated with one another will be treated as a single entity. By using PCA, it thus will be possible to obtain a small set of uncorrelated variables still representing most of the information which was present in the original set of variables, but being far easier to use in models. In general, 2 to 15 principal components will account for 85% to 98% of the variance of the variables. Another embodiment includes the transformation of spectral data into principal components (with or without data processing) and thus monitoring the principal components as function of time and relating these values to parameters commonly used for process control.

(I.c.2) Partial Least Squares Regression (PLS)

PLS is a modelling and computational method by which quantitative relations can be established between blocks of variables, e.g. a block of descriptor data (spectrum) for a series of samples and a block of response data measured on these samples. By the quantitative relation between the blocks, it is possible to enter spectral data for a new sample to the descriptor block and make predictions of the expected responses. One great advantage of the method is that the results can be evaluated graphically, by different plots. In most cases, visual interpretations of the plot are sufficient to obtain a good understanding of different relations between the variables. The method is based upon projections, similar to PCA. The PLS method is disclosed in detail in Carlsson R., Design and optimization in organic synthesis, B.G.M. Vandeginste, O. M. Kvalheim, Eds., Data handling in science and technology, (Elsevier, 1992), vol.8.

12

(I.c.3) Principal Components Regression (PCR)

PCR is closely related to PCA and PLS. As in PCA, each object in the descriptor block is projected onto a lower dimensional space yielding in scores and loadings. The scores are then regressed against the response block in a least squares procedure leading to a regression model which can be used to predict unknown samples. The same model statistics as in PLS and PCA can be used to validate the model.

For an exellent tutorial in PCA, PLS and PCR, see P. Geladi et al in "Partial Least-Squares Regression: A Tutorial" in Anal. Chim. Acta, 185, 1-32 (1986), which is incorporated herein by reference in its entirety.

(I.c.4) Multilinear Regression Analysis (MLR)

By MLR, the best fitting plane for the kappa number as a function of the spectra is defined, using least squares techniques to define each boundary of the plane. This plane is then used to recognize and assign a predicted value to an unknown kappa number. This technique is generally limited to relatively 'clean' systems where there is not a significant amount of matrix interference and, in contrast to PLS, it requires more objects than variables.

(I.c.5) Discriminant Analysis

This is a method whereby, by use of spectral data, the known kappa number values are grouped into different clusters, separated by linear decision boundaries. From its spectrum, a sample of unknown kappa number then can be matched to a cluster, and the kappa number can be assigned a value, e.g. the average value of the cluster. This is a very useful technique for quality screening, but requires a very large data base to obtain statistically significant results.

13

(II) DETERMINATION OF THE ORGANIC MATERIAL BY APPLICATION OF
THE CALIBRATION MODEL.

Once a calibration model has been developed, the determination
of the unknown kappa number can be performed by registering
the absorption, transmittance or reflectance spectrum, in
correspondence to (I.a), from the pulp mill effluent of the
unknown kappa number; processing the thereby obtained spectral
raw data as according to (I.b); optionally performing a data
analysis on the processed spectral data as according to (I.c);
and applying the developed calibration model to the thereby
obtained data.

The invention will now be illustrated by way of an example.

EXAMPLE

Multiwavelength spectroscopy, carried out on the effluents
from bleaching pulp, followed by linearisation of spectral
data and multivariate data evaluation (PLS algorithm) were
used to determine the reduction in kappa number before and
after bleaching. The organic content is expressed as kappa
number reduction between two bleaching stages.

DEVELOPMENT OF A CALIBRATION MODEL
(A) Development of learning sets
SAMPLES
The reference samples consisted of in total 55 effluents from
bleaching chemical pulp, originating from different sites in
the bleaching sequence, and thereby having different pHs and
COD levels. The samples had been treated in different
bleaching sequences and the kappa number was determined for
each sample, using the TAPPI Standard Method T 236 cm-85.

UV ABSORBANCE MEASUREMENTS
The UV measurements were obtained using a Spectra Focus®
Optical Scanning Detector (Spectra-Physics), equipped with a
fused silica capillary with an inner diameter of 0.53 mm as
the flow through cell. Measurements were made directly on the

14

capillary, on which a 10 mm window had been obtained, by
burning off the polymer coating. The samples were pumped
through the capillary by means of a peristaltic pump (Gilson
Minipuls 2) at a speed of 2.4 ml min^{-1}. A spectral operating
range between 200 nm and 360 nm, in even intervals of 2 nm,
was used, yielding 81 measurements at different wavelengths.
Four measurements were made on each sample, and their mean
spectrum was calculated and used in further evaluations. The
absorbance data obtained were transferred to an IBM PS-2 7386
computer equipped with the Autolab® Software (Spectra-Phy-
sics).

(B) Data processing
The whole spectral data matrix was used for modelling, which
resulted in 81 spectral points.

LINEARISING TRANSFORMATION
Two linearising functions were tried, i.e. 2nd derivative and
MSC on the original spectra. Models were built on both the
original data matrix, as well as on the transformed.

(C) Data analysis
The commercially available MATLAB software V 4.0 was used for
numerical calculations. The PLS-algorithm used for modelling
the relationships between the spectra and descriptors is a
customised function in the PLS Toolbox, made by Barry M. Wize
(free available) based on the NIPALS algorithm (H. Wold, P.
Krishnaiah, Multivariate Analysis, 391 (1966)). The metod of
establishing the significant number of PLS-components was
crossvalidation (S. Wold, Technometrics 20, 397-405 (1978))
(Jack-knifing) with one sample left out. This procedure was
repeated in an iterative manner, leaving out another sample,
so that each predicted value was based on a model in which the
predicted sample was not present. The values from the refer-
ence method were mean-centered and optionally scaled to unit
variance prior to modelling (autoscaling or z-transform) and
rescaled prior to model evaluatiIn order to facilitate a

15

further understanding of the invention, the following examples
are presented primarily for the purpose of illustrating
certain more specific details thereof. The invention is not to
be limited thereby except as defined in the claims.

RESULTS

The measured vs. modelled values of the reduction in the kappa
number are plotted in Fig. 1. As can be seen the deviation
from the theoretical value, represented in the figure as a
straight line is minimal.

In Fig. 1 and 2 the values from the reference methods, are
plotted vs. the values, calculated by the model (predicted
values). Data pretreatment were multiplicative scatter
correction and mean centering. Solid line denotes slope 1.0,
dashed line was fitted with linear regression, while dotted
lines denote the confidence limit at the 95% significance
level (SEP = Standard error of prediction; RMSECV = Root mean
squared error of cross validation; MSECV = Mean squared error
of cross validation; INTER = intercept; K = slope; r∧2 = the
square of the correlation coefficient for the fitted dashed
line).

Figur 1 shows the prediction of kappa number using a PLS model
with 7 principal componenents.

Figur 2 shows the prediction of COD using a PLS model with 3
principal components.

Ideally, the slope of the line (k) and its correlation coeffi-
cient (r^2) should be as close to 1 as possible; while the
intercept should be as close to 0 as posssible. In view of the
values obtained, it will be possible to realize the very good
validity and precision of the model.

The advantage of the novel method of monitoring organic con-
tent in pulp or pulp mill effluent using chemometrics, should

16

thus be readily apparent. Indeed, a wide variety of samples, originating from various pulp mills and production processes, may be analysed using the same calibration set. The invention thus provides a method whereby the monitoring of the quality of pulp and of the organic content in effluents from pulp and paper mill production process can be performed in a very rapid and precise way on any type of pulp and paper.

17

CLAIMS

1. A method for qualitative and quantitative determination of
the organic content in effluents from pulp and paper
production by
(I) developing a calibration model by
(I.a) registering absorption, transmittance or reflectance
spectra of reference samples of known properties and
concentration of organic substances to develop learning sets;
(I.b) processing the spectral raw data, to reduce noise and
adjust for drift and diffuse light scatter;
(I.c) performing a data analysis by applying chemometric
techniques to the processed learning sets; and thus calibra-
ting the processed spectral data with the actual values
obtained from reference analytical methods;
(II) determining the unknown properties and/or organic sub-
stances of pulp and paper by registering the absorption,
transmittance or reflectance spectra, in correspondence to
(I.a); processing the thereby obtained spectral raw data as
according to (I.b); and applying the developed calibration
model to the processed data,
c h a r a c t e r i z e d in the qualitative and quantitative
determination of the parameters reflecting the quality of pulp
or paper and the environmental impact of the effluents by
measuring the organic content in the aqueous phase, obtained
in pulp and paper production.

2. A method according to Claim 1, c h a r a c t e r i z e d in
the calculation of the difference in the product quality be-
fore and after a process stage, and qualitatively and quanti-
tatively relating this value to the spectral information,
obtained by measuring the process effluent.

3. A method according to Claim 2, c h a r a c t e r i z e d in
the calculation of the difference in kappa number before and
after a bleaching stage, and quantitatively relating this

value to the selected part of the spectral information, obtained by measuring the bleach plant effluent.

4. A method according to Claim 2, c h a r a c t e r i z e d in the calculation of the difference in paper strength, measured as the viscosity value, before and after a bleaching stage, and quantitatively relating this value to the selected part of the spectral information, obtained by measuring the bleach plant effluent.

5. A method according to Claim 2, c h a r a c t e r i z e d in the calculation of the difference in paper strength, measured as tear index, tensile index, burst index and similar parameters, before and after a bleaching stage, and quantitatively relating this value to the selected part of the spectral information, obtained by measuring the bleach plant effluent.

6. A method according to Claim 2, c h a r a c t e r i z e d in the calculation of the difference in paper whiteness or brightness, measured as ISO-90 or similar parameters, before and after a bleaching stage, and quantitatively relating this value to the selected part of the spectral information, obtained by measuring the bleach plant effluent.

7. A method according to Claim 1, c h a r a c t e r i z e d in the determination of organic content in pulp and paper process effluents, and qualitatively and quantitatively relating this value to selected parts of the spectral information, obtained from the process effluent.

8. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the organic content, defined as chemical oxygen demand (COD), in the aqueous effluent from pulp mill or paper mill production, and quantitatively relating the COD value to selected parts of the spectral information, obtained from the effluent.

19

9. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the organic content, defined as total organic carbon content (TOC), in the aqueous effluent from pulp mill or paper mill production, and quantitatively relating the TOC value to selected parts of the spectral information, obtained from the effluent.

10. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the organic content, defined as biological oxygen demand (BOD), e.g. BOD 5, BOD 7 and BOD 28, in the aqueous effluent from pulp mill or paper mill production, and quantitatively relat- ing the BOD value to selected parts of the spectral information, obtained from the effluent.

11. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the organic content, defined as adsorbable organic halogenates (AOX), in the aqueous effluent from pulp mill or paper mill production, and quantitatively relating the AOX value to selected parts of the spectral information, obtained from the effluent.

12. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the organic content, defined as one or several groups related to their chemical structures e.g. extractives, lignin residues and/or carbohydrates.

13. A method according to Claim 7, c h a r a c t e r i z e d in the determination of suspended solids in the aqueous effluent from pulp mill or paper mill production, and quantitatively relating the value of suspended solids to selected parts of the spectral information, obtained from the effluent.

14. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the colour in the aqueous effluent from pulp mill or paper mill production, and quantitatively

relating the COD value to selected parts of the spectral information, obtained from the effluent.

15. A method according to Claim 7, c h a r a c t e r i z e d in the determination of the wash losses, defined as chemical oxygen demand (COD) or sodium sulphate, in the aqueous effluent from pulp mill or paper mill production, and quantitatively relating the wash losses to selected parts of the spectral information, obtained by measuring the effluent.

16. A method according to Claim 1, c h a r a c t e r i z e d in the calculation of principal components and relating the values as obtained as a function of time to known qualitativa or quantitative parameters used for process control.
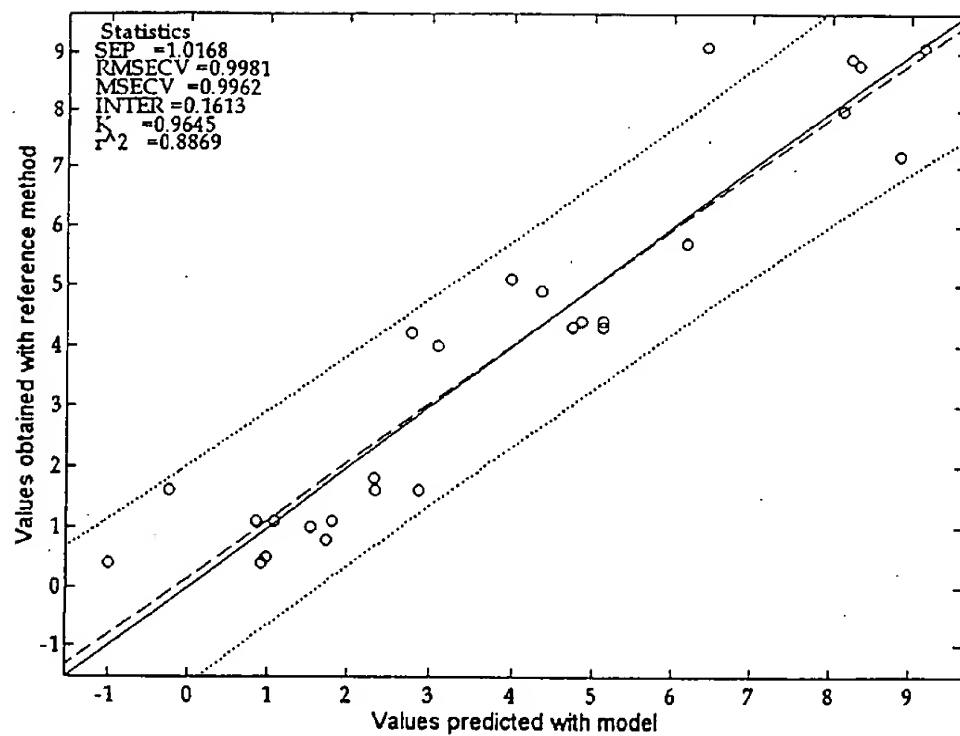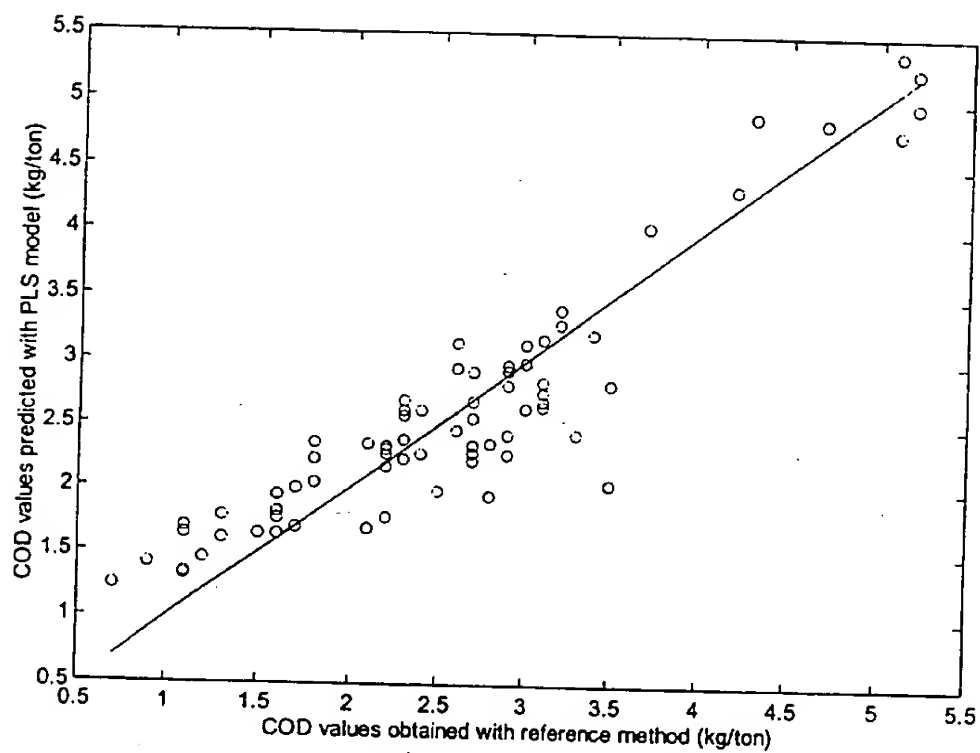
FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   G01N33/34   D21C9/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,4 743 339 (FAIX) 10 May 1988 see abstract see column 1, line 58 - column 2, line 2 see column 2, line 13 - line 39 see column 2, line 34 - line 39 ---	1-3,7, 12,16
Y	EP,A,0 559 305 (W.R. GRACE) 8 September 1993 see abstract see page 5, line 39 - line 40 see page 7, paragraph 1 see claims 1,3,12,14 & US,A,5 242 602 cited in the application ---	1-3,7, 12,16

-/--

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

Date of the actual completion of the international search	Date of mailing of the international search report
20 February 1996	2 8. 02 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Thomas, R.M.

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 344 694 (HERCULES) 6 December 1989 see abstract see page 2, line 39 - line 49 see page 5, line 45 - line 57 see page 6, line 7 - line 10 see claims 1-5,11-15 ---	1,2
A	WO,A,94 01769 (PULP & PAPER RESEARCH INSTITUTE OF CANADA) 20 January 1994 see abstract; figure 6; example 3 ---	1,2
A	WATER, AIR & SOIL POLLUTION, vol. 39, May 1988 pages 75-80, XP 000563576 R.K. SRIVASTAVA ET AL 'Water quality along the Sone river polluted by the Orient paper mill' see abstract see page 76, last two lines -----	1,7,8, 10,13

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4743339	10-05-88	DE-A-	3616051	19-11-87
		CA-A-	1277110	04-12-90
		DE-A-	3687658	11-03-93
		EP-A,B	0245536	19-11-87
EP-A-0559305	08-09-93	US-A-	5242602	07-09-93
		AU-B-	3319793	09-09-93
		CA-A-	2090820	05-09-93
		CN-A-	1079301	08-12-93
		JP-A-	6066718	11-03-94
		NZ-A-	245904	28-03-95
		ZA-A-	9301218	17-09-93
EP-A-0344694	06-12-89	JP-A-	2035338	05-02-90
		US-A-	5104485	14-04-92
WO-A-9401769	20-01-94	US-A-	5282931	01-02-94
		AU-B-	4554693	31-01-94
		CA-A-	2138048	20-01-94
		EP-A-	0649531	26-04-95
		FI-A-	950078	05-01-95
		JP-T-	7508834	28-09-95
		US-A-	5378320	03-01-95
		US-A-	5364502	15-11-94